SUMMARY PROBLEM

(a) $CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$ $\qquad K = \dfrac{P_{CH_3OH}}{(P_{CO})\,(P_{H_2})^2}$

(b) $K = \dfrac{0.0134}{(0.702)(1.75)^2} = 6.23 \times 10^{-3}$

(c) $K' = \left(\dfrac{1}{K}\right)^{\frac{1}{2}} = \left(\dfrac{1}{6.23 \times 10^{-3}}\right)^{\frac{1}{2}} = 12.7$

(d) $P_{H_2} = 2P_{CO}$ $\qquad 6.23 \times 10^{-3} = \dfrac{0.0300}{(P_{CO})\,(2P_{CO})^2}$; $\qquad P_{CO} = 1.06$ atm; $P_{H_2} = 2.12$ atm

(e) $\Delta H^o = -201.2 - [(-110.6) + 2(0)] = -90.6$ kJ

$$\ln \frac{K_2}{6.23 \times 10^{-3}} = \frac{-90.7}{0.00831}\left(\frac{1}{500} - \frac{1}{323}\right); \qquad K_2 = 976$$

(f) (1) $\rightarrow$ (2) no change (3) $\leftarrow$ (4) $\leftarrow$

(g)

	$CO(g)$	+	$3H_2(g)$	$\rightleftharpoons$	$CH_4(g)$	+	$H_2O(g)$
P_o	0		0		1.00		1.00
ΔP	$+x$		$+3x$		$-x$		$-x$
P_{eq}	x		$3x$		$1.00 - x$		$1.00 - x$

$$2.57 = \frac{(1.00 - x)(1.00 - x)}{(x)(3x)^3} = \frac{(1.00 - x)^2}{27x^4}$$

$$\left[(2.57)(27x^4)\right]^{\frac{1}{2}} = \left[(1.00 - x)^2\right]^{\frac{1}{2}}; \qquad x = P_{CO} = 0.292 \text{ atm}$$

$P_{H_2} = 3(0.292) = 0.876$ atm

$P_{CH_4} = P_{H_2O} = 1.00 - 0.292 = 0.708$

PROBLEMS

1. (a) ≈ 80 s (b) faster at 30 s; equal at 90 s

3.

t(s)	10	20	30	40	50	60
P_A (atm)	2.000	1.625	1.325	1.100	0.950	0.950
P_B (atm)	1.200	0.950	0.750	0.600	0.500	0.500
P_C (atm)	0.150	0.275	0.375	0.450	0.500	0.500

5. (a) $K = \frac{(P_{IF_5})^2}{(P_{I_2})(P_{F_2})^5}$ (b) $K = \frac{1}{(P_{CO})(P_{H_2})^2}$

(c) $K = \frac{(P_{SO_2})^2}{(P_{H_2S})^2(P_{O_2})^3}$ (d) $K = \frac{1}{(P_{H_2})^2}$

7. (a) $K = \frac{(P_{NO})^2[Cu^{2+}]^3}{[NO_3^-]^2[H^+]^8}$ (b) $K = \frac{(P_{SO_2})^2}{(P_{O_2})}$ (c) $K = \frac{1}{[Ca^{2+}][CO_3^{2-}]}$

9. (a) $N_2(g) + Na_2CO_3(s) + 4\,C(s) \rightleftharpoons 3\,CO(g) + 2\,NaCN(s)$; $K = \frac{(P_{CO})^3}{(P_{N_2})}$

(b) $Mg_3N_2(s) + 6\,H_2O(g) \rightleftharpoons 3\,Mg(OH)_2(s) + 2\,NH_3(g)$; $K = \frac{(P_{NH_3})^2}{(P_{H_2O})^6}$

(c) $NH_4^+(aq) + OH^-(aq) \rightleftharpoons NH_3(aq) + H_2O$; $K = \frac{[NH_3]}{[NH_4^+][OH^-]}$

11. (a) $C_3H_8(g) + 5\,O_2(g) \rightleftharpoons 3\,CO_2(g) + 4\,H_2O(g)$

(b) $2\,C_5H_6(g) \rightleftharpoons C_{10}H_{12}(g)$

(c) $H_3PO_4(aq) \rightleftharpoons 3\,H^+(aq) + PO_4^{3-}(aq)$

(d) $CO_3^{2-}(aq) + 2\,H^+(aq) \rightleftharpoons CO_2\,(g) + H_2O(g)$

13. (a) $K_1 = \frac{(P_D)^2}{(P_B)^2}$ (b) $K_2 = \frac{P_B}{P_D}$ (c) $K_2 = \left(\frac{1}{K_1}\right)^{\frac{1}{2}}$ or $K_1 = \left(\frac{1}{K_2}\right)^2$

15. (a) $K = (2.2 \times 10^{-3})^2 = 4.8 \times 10^{-6}$ (b) $K = \frac{1}{4.8 \times 10^{-6}} = 2.1 \times 10^5$

17.

$Fe(s) + CO_2(g) \rightleftharpoons FeO(s) + CO(g)$	$K = 1/0.67$
$H_2O(g) + CO(g) \rightleftharpoons H_2(g) + CO_2(g)$	$K = 1.6$
$Fe(s) + H_2O(g) \rightleftharpoons FeO(s) + H_2(g)$	$K = 1.6/0.67 = 2.4$

19.

$N_2O(g) \rightleftharpoons N_2(g) + \frac{1}{2}\,O_2(g)$	$K_1 = 1/(1.2 \times 10^{-35})^{\frac{1}{2}}$
$2\,NO_2(g) \rightleftharpoons N_2O_4(g)$	$K_2 = 1/(4.6 \times 10^{-3})$
$N_2(g) + 2\,O_2(g) \rightleftharpoons 2\,NO_2(g)$	$K_3 = (4.1 \times 10^{-9})^2$
$N_2O(g) + \frac{3}{2}\,O_2(g) \rightleftharpoons N_2O_4(g)$	$K = \frac{(4.1 \times 10^{-9})^2}{(1.2 \times 10^{-35})^{\frac{1}{2}}(4.6 \times 10^{-3})} = 1.1 \times 10^3$

21. $K = \dfrac{(0.0391)(0.0124)}{(0.921)(1.21)^3} = 2.97 \times 10^{-4}$

23. (a) $NH_4CO_2NH_2(s) \rightleftharpoons 2\,NH_3(g) + CO_2(g)$ (b) $K = (0.0451)(0.0961)^2 = 4.16 \times 10^{-4}$

25. $(0.692)(0.124) = 0.0858 = \Delta P$

	$NH_4HS(s)$	$\rightleftharpoons$	$NH_3(g)$	+	$H_2S(g)$
P_o			0.692		0.0532
ΔP			+ 0.0858		+ 0.0858
P_{eq}			0.778		0.139

$K = (0.778)(0.139) = 0.108$

27. (a) $Q = \dfrac{(0.30)(0.16)}{0.50} = 0.096 > 0.011$; no (b) reverse direction

29. (a) $Q = 0$; $\rightarrow$ (b) $Q = \dfrac{(0.2)^2(0.35)^2}{(0.30)^4(0.15)} = 4$; $\leftarrow$

31. $Q = \dfrac{(0.250)(0.250)^3}{(0.250)^2} = 0.0625 > 1.1 \times 10^{-3}$; $\leftarrow$

33. $0.0049 = \dfrac{(0.213)^2(0.883)^6}{(0.255)^3(P_{NH_3})^4}$; $P_{NH_3} = 4.0$ atm

35. $1.3 \times 10^5 = \dfrac{(P_{H_2S})^2}{(0.103)^2(0.417)}$; $P_{H_2S} = 24$ atm

37. $P_{TOT} = P_{N_2} + P_{NO} + P_{H_2} + P_{H_2O}$; $P_{H_2} + P_{H_2O} = 1.87 - (0.168 + 0.225) = 1.48$ atm

$P_{H_2} = 1.48 - P_{H_2O}$

$1.54 \times 10^{-3} = \dfrac{(0.225)^2(1.48 - P_{H_2O})^2}{(0.168)(P_{H_2O})^2}$; $P_{H_2O} = 1.38$ atm ; $P_{H_2} = 0.10$ atm

39. $CO(g) + CF(g) \rightleftharpoons 2\,COF(g)$

	$CO(g)$	$CF(g)$	$2\,COF(g)$
P_o	0.713	0.713	0
ΔP	$-x$	$-x$	$+2x$
P_{eq}	$0.713 - x$	$0.713 - x$	$2x$

$0.50 = \dfrac{(2x)^2}{(0.713 - x)^2}$; $x = 0.19$; $P_{COF_2} = 0.38$ atm ; $P_{CO_2} = P_{CF_4} = 0.52$ atm

41. $CO(g) + H_2O(g) \rightleftharpoons H_2(g) + CO_2(g)$

	$CO(g)$	$H_2O(g)$	$H_2(g)$	$CO_2(g)$
P_o	0.485	0.485	0.159	0.159
ΔP	$-x$	$-x$	$+x$	$+x$
P_{eq}	$0.485 - x$	$0.485 - x$	$0.159 + x$	$0.159 + x$

(a) $1.30 = \dfrac{(0.159 + x)^2}{(0.485 - x)^2}$; $x = 0.184$; $P_{H_2} = P_{CO_2} = 0.343$ atm ; $P_{H_2O} = P_{CO} = 0.300$ atm

$P_{tot} = 1.288$ atm originally; 1.286 finally (same)

no; only if number of moles of gas remains unchanged

43. (a) $(P_{NH_3})^2(P_{CO_2}) = 2.3 \times 10^{-4}$; $P_{NH_3} = 2P_{CO_2}$; $4(P_{CO_2})^2 = 2.3 \times 10^{-4}$

$P_{CO_2} = 3.9 \times 10^{-2}$ atm ; $P_{NH_3} = 7.7 \times 10^{-2}$ atm ; $P_{tot} = 0.116$ atm

(b) mol $NH_4CO_2NH_2$ decomposed = mol CO_2 = $\dfrac{(3.9 \times 10^{-2}\ \text{atm})(10.0\ \text{L})}{(0.0821\ \text{L} \cdot \text{atm/mol} \cdot \text{K})(298\ \text{K})} = 0.016$

mass $NH_4CO_2NH_2$ decomposed = (0.016 mol)(78.1 g/mol) = 1.2 g

% $NH_4CO_2NH_2$ decomposed = $\dfrac{1.2}{7.5} \times 100 = 16\%$

(c) no; unrelated

45. $2\,HCN(g) \rightleftharpoons C_2N_2(g) + H_2(g)$

	$2\,HCN(g)$	$C_2N_2(g)$	$H_2(g)$
P_o	0.45	0.32	0.32
ΔP	$+2x$	$-x$	$-x$
P_{eq}	$0.45 + 2x$	$0.32 - x$	$0.32 - x$

$0.17 = \frac{(0.32 - x)^2}{(0.45 + 2x)^2}$; $x = 0.08$ atm ; $P_{C_2N_2} = P_{H_2} = 0.24$ atm ; $P_{HCN} = 0.60$ atm

47. (a) $P_{products}$ increases (b) $P_{reactants}$ increases (c) $P_{reactants}$ increases

49. (a) (1) ← (2) ← (3) no effect (4) → (5) →

(b) Decreasing T decreases K

51. (a) ← (b) ← (c) no effect

53. (a) $K = \frac{(0.022)^2}{(1.2)(0.80)} = 5.0 \times 10^{-4}$

(b)

	$N_2(g)$	+	$O_2(g)$	$\rightleftharpoons$	$2\,NO(g)$
P_o	1.2		1.2		0.022
ΔP	$-x$		$-x$		$+2x$
P_{eq}	$1.2 - x$		$1.2 - x$		$0.022 + 2x$

$5.0 \times 10^{-4} = \frac{(0.022 + 2x)^2}{(1.2 - x)(1.2 - x)}$; $x = 0.0020$ atm ; $P_{NO} = 0.026$ atm ; $P_{N_2} = P_{O_2} = 1.198$ atm

55. (a) $K = \frac{(0.16)(0.27)}{(0.43)^2} = 0.23$

(b) →

	$2\,ICl(g)$	$\rightleftharpoons$	$I_2(g)$	+	$Cl_2(g)$
P_o	0.43		0.10		0.27
ΔP	$-2x$		$+x$		$+x$
P_{eq}	$0.43 - 2x$		$0.10 + x$		$0.27 + x$

$0.23 = \frac{(0.10 + x)(0.27 + x)}{(0.43 - 2x)^2}$; $x = 0.02$ atm ; $P_{I_2} = 0.12$ atm

57. $\ln \frac{62.5}{K} = \frac{-9.4\text{ kJ/mol}}{0.00831\text{ kJ/mol}\cdot\text{K}}\left(\frac{1}{606\text{ K}} - \frac{1}{800\text{ K}}\right)$; $K = 98$

59. $\ln \frac{K_2}{K_1} = \frac{33\text{ kJ/mol}}{0.00831\text{ kJ/mol}\cdot\text{K}}\left(\frac{1}{200\text{ K}} - \frac{1}{400\text{ K}}\right)$; $\frac{K_2}{K_1} = 2.0 \times 10^4$

61. $200 = \frac{[\text{HbCO}]P_{O_2}}{[\text{HbO}_2]P_{CO}}$; $200 = \frac{0.21}{P_{CO}}$; $P_{CO} = 1.0 \times 10^{-3}$ atm

63. $P_{O_2} = \frac{(1 \text{ mol})(0.0821 \text{ L} \cdot \text{atm/mol} \cdot \text{K})(1800 \text{ K})}{5.0 \text{ L}} = 29.6$ atm; $\frac{(P_O)^2}{29.6} = 1.7 \times 10^{-8}$; $P_O = 7.1 \times 10^{-4}$ atm

mol O $= \frac{(7.1 \times 10^{-4} \text{ atm})(5.0 \text{ L})}{(0.0821 \text{ L} \cdot \text{atm/mol} \cdot \text{K})(1800 \text{ K})} = 2.4 \times 10^{-5}$

mol O_2 after dissociation = $\frac{1}{2}(2.4 \times 10^{-5}) = 1.2 \times 10^{-5}$

mass O_2 = $(1.2 \times 10^{-5}$ mol)(32 g/mol) $= 3.8 \times 10^{-4}$ g

% dissociated = $\frac{3.8 \times 10^{-4}}{32} \times 100 = 1.2 \times 10^{-3}$ %

O atoms = $(2.4 \times 10^{-5}$ mol)$(6.022 \times 10^{23}$ atoms/mol) $= 1.4 \times 10^{19}$

65. mol C_3H_7OH = (20.0 mL)(0.785 g/mL)(1 mol/60.1 g) = 0.261

$P_o = \frac{(0.261 \text{ mol})(0.0821 \text{ L} \cdot \text{atm/mol} \cdot \text{K})(453 \text{ K})}{5.00 \text{ L}} = 1.94$ atm

	C_3H_7OH	$\rightleftharpoons$	C_2H_6O	+	H_2
P_o	1.94		0		0
ΔP	$-x$		$+x$		$+x$
P_{eq}	$1.94 - x$		x		x

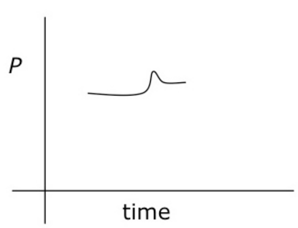
$0.45 = \frac{(x)(x)}{(1.94 - x)}$; $x = 0.74$ atm ; undissociated $C_3H_7OH = 1.94 - 0.74 = 1.20$ atm

% undissociated $C_3H_7OH = \frac{1.20}{1.94} \times 100 = 62\%$

67. (a) Point 1: $Q = K$; Point 3: $Q = K$; Point 4: $Q > K$

(b) P increased by compression, equilibrium shifts to the left.

(c)



69. (a) $P_A = 0.75$ atm ; $P_B = 0.50$ atm (b) 0.62 atm (c) 0.60 atm

71. (a) EQ (b) GT (c) MI (d) EQ (e) EQ

(f) EQ (g) MI (h) MI (i) EQ

73. b or c (intermediate between 1.5 and 0.44)

75. Position of equilibrium is independent of rate.

77.

	$2\,NO$	+	O_2	$\rightleftharpoons$	$2\,NO_2$
P_o	0.81		0.70		0
ΔP	$-2x$		$-x$		$+2x$
P_{eq}	$0.81 - 2x$		$0.70 - x$		$2x$

$P_{tot} = P_{NO} + P_{O_2} + P_{NO_2}$; $1.20 = (0.81 - 2x) + (0.70 - x) + 2x$; $x = 0.31$ atm

$P_{NO} = 0.19$ atm ; $P_{O_2} = 0.39$ atm ; $P_{NO_2} = 0.62$ atm

$$K = \frac{(0.62)^2}{(0.19)^2(0.39)} = 27$$

78. $a\,A(g) + b\,B(g) \rightleftharpoons c\,C(g) + d\,D(g)$; $P_A = [A]RT$; $(P_A)^a = [A]^a(RT)^a$

$$K = \frac{(P_C)^c(P_D)^d}{(P_A)^a(P_B)^b} = \frac{[C]^c[D]^d}{[A]^a[B]^b} \times (RT)^{(c+d-a-b)} = K_c(RT)^{\Delta n_g}$$

79. $2.5 = \dfrac{(x)(3x)^3}{(1-2x)^2}$; $(2.5)^{\frac{1}{2}} = \left(\dfrac{27x^4}{(1-2x)^2}\right)^{\frac{1}{2}}$; $1.6 = \dfrac{5.2x^2}{1-2x}$; $x = 0.33$ atm

$P_{N_2} = 0.33$ atm ; $P_{H_2} = 0.99$ atm ; $P_{NH_3} = 0.34$ atm

80. mol $Na_2S_2O_3$ = (0.200 mol/L)(0.0370 L) = 0.00740

mol $I_2 = \frac{1}{2}$(mol $Na_2S_2O_3$) = 0.00370 ; $P_{I_2} = 0.00370\,\dfrac{RT}{V}$; $P_{H_2} = P_{I_2} = 0.00370\,\dfrac{RT}{V}$

mol HI at the start: = $\dfrac{3.20\text{ g}}{127.9\text{ g/mol}}$ = 0.0250 ; mol HI at the end = 0.0250 − 2(mol I_2) = 0.0176

$$P_{HI} = 0.0176\,\frac{RT}{V}$$

$$K = \frac{[0.00370\,(RT/V)][0.00370\,(RT/V)]}{[0.0176\,(RT/V)]^2} = 0.0442$$

81. Let x equal decrease in SO_3 pressure ; $0.45 = \dfrac{x(\sqrt{x/2})}{1.00 - x}$; $x = 0.48$ atm ; $P_{SO_3} = 0.52$ atm

82. Let P_o of $I_2 = 1.00$ atm; $x = \Delta P_{I_2}$; $P_{tot} = 1.40$; $1.40 = 1.00 - x + 2x$; $x = 0.40$ atm

At equilibrium: $P_{I_2} = 0.60$ atm, $P_I = 0.80$ atm ; $K = \dfrac{(0.80)^2}{0.60} = 1.1$

83. At equilibrium: $P_{XeF_4} = 0.10$ atm ; $P_{Xe} = 0.10$ atm ; $P_{F_2} = 0.20$ atm

$$K = \frac{0.10}{(0.10)(0.20)^2} = 25$$

New equilibrium pressures: $P_{XeF_4} = 0.15$ atm ; $P_{Xe} = 0.05$ atm

$25 = \dfrac{0.15}{(0.05)(P_{F_2})^2}$; $P_{F_2} = 0.35$ atm ; $P_{initial} = 0.35 \text{ atm} + 2(0.15 \text{ atm}) = 0.65$ atm

84. (a) P_o for $C_6H_5CH_2OH = \dfrac{(1.50 \text{ g}/108.13 \text{ g/mol})(0.0821 \text{ L} \cdot \text{atm/mol} \cdot \text{K})(523 \text{ K})}{2.0 \text{ L}} = 0.30$ atm

$0.56 = \dfrac{x^2}{0.30 - x}$; $x = 0.22$; P_{eq} for benzaldehyde = 0.22 atm

(b) P_{eq} for benzyl alcohol = 0.08 atm

moles benzyl alcohol = $\dfrac{(0.08 \text{ atm})(2.0 \text{ L})}{(0.0821 \text{ L} \cdot \text{atm/mol} \cdot \text{K})(523 \text{ K})} = 0.004$

mass = (0.004 mol)(108.13 g/mol) = 0.4 g